TOPOGRAPHY OF REACTION SPACE DURING INDUCED FORMATION OF FINE-CRYSTALLINE CORUNDUM IN SCWF

Yu.D. Ivakin*, M.N. Danchevskaya, G.P. Muravieva
M.V. Lomonosov Moscow State University, Russia
Ivakin@kge.msu.ru

ABSTRACT The formation of fine-crystalline corundum from hydrargillite at 400° C in supercritical water fluid (SCWF) at a pressure of 26.8 MPa in the presence of α-Al_2O_3 particles is investigated. It was found that the addition of fused α-Al_2O_3 particles into the reaction medium accelerates the formation of fine-crystalline corundum by the increase of the nucleation rate. The process is accompanied by both the build-up of fused corundum grains, and the generation of new corundum crystals from boehmite. It was found that the formation of new crystals depends on the distance between grains of additives. Depending on this distance, the newly formed crystals consist of two or three fractions with different average particle size. It is concluded that the build-up of fused corundum particles in the medium of SCWF occurs due to the uptake of corundum nuclei, formed in the surrounding layer of boehmite. Added particles of fused corundum with average size of 2.82 micrometers have the layer of a thickness of 17.47 microns from which the build-up occurs. Corundum nuclei formed at large distances from the growing particles become centers of growth of new corundum crystals of the smallest sizes. SCWF role is to increase the spatial and structural mobility of the reactants.

INTRODUCTION

Treatment of hydrargillite, γ-$Al(OH)_3$, with a water fluid (at 400ºC and 26.8 MPa) results in solid restricting with formation of well faceted corundum microcrystals [1]. The synthesis of corundum involves the intermediate formation of boehmite. Transformation proceeds according to the equation $2Al(OH)_3 \rightarrow 2AlOOH + 2H_2O \rightarrow Al_2O_3 + 3H_2O$ and 1 g hydrargillite converted into 0.654 g of corundum. The kinetics of boehmite into corundum transformation is described by the Erofeev equation for the case of chain nucleation [2]:

$$\alpha = 1 - \exp\{-\exp(k_N t + c) + \exp c\}, \qquad (1)$$

where α is the conversion degree of boehmite into corundum, k_N is the rate constant for the corundum nucleation. The peculiarity of chain nucleation mechanism is that the formed nucleus induces the formation of new nuclei. The literature describes the use of α-Al_2O_3 seed to accelerate the conversion and the effect on crystal size of the product during the corundum synthesis under hydrothermal [3, 4], solvothermal [5] or high-temperature [6] conditions. The aim of this work has been study the mechanism of the effect of added α-Al_2O_3 particles on corundum formation in a supercritical water fluid of low density (28 MPa, 400ºC). Under these conditions, the alumina is not soluble in the water fluid [7] and the transformation of hydrargillite into corundum proceeds by solid phase mechanism [2].

MATERIALS AND METHODS

Corundum was synthesized from finely dispersed hydrargillite produced at Pikalevsk alumina plant. Mean particle size of hydrargillite is $3,46 \pm 0,06$ μm, the bulk density of 0.65 g/cm^3 at free backfill and 1.2 g/cm^3 at seal. Inducing additive particles were crystalline powder white

fused alumina M5. The mixture of components was sieved through a capron sieve of 300 microns four times for a uniform distribution of additives. The reaction mixture was placed in a stainless steel container with loose backfill. Distilled water was poured on bottom of the autoclave below the container placed on stand. The autoclave was heated to 400° C and withstands the required time. Fill Factor water space of the autoclave was 20%, which is at 400°C corresponds to 26.8 MPa. The phase composition of the synthesized products was investigated using a STOE-1P diffractometer with Cu $K\alpha$-radiation. The size and morphology of crystals were studied using a JSM-639OLA and Cam Scan Series 2 scanning electron microscopes. Crystal size distribution for synthesized samples was determined by analyzing by linear segments of SEM images of several sections for each sample. The amount of additive is represented as the mass ratio of the additive and corundum formed from hydrargillite: $K = M_{additive}/M_{hydrargillite} \times 0.654$. In this work, the amount of additive varied from $K=0.00076$ to $K=0.013$. The number of grains (n_a) in a mass of additive (M, g) was calculated by the equation $n_a = M_{additive}/m = 6 \cdot M_{additive}/\pi \ d_a^3 \cdot 3.99 \cdot 10^{-12}$, where 3.99 g/cm^3 is the true density of corundum and d_a, μm is the mean grain diameter of additive with mass m, g. Distance (D, μm) between the grains of additive, which are uniformly distributed in the reaction mixture, is calculated on the assumption that the volume of the reaction mixture (V = $M_{hydrargillite}/\rho + M/3.99$) consists of $n_a = g \cdot 6V/\pi D^3$ conditional spheres of diameter D, μm. The coefficient g takes into account the disordered space filling by spheres and equal to 0.64 [8]. Under these conditions, $D = d_a \cdot [g(3.99/\rho \cdot K \cdot 0.654 + 1)]^{1/3}$ or when the bulk density of the reaction mixture $\rho=0.65$ g/cm^3:

$$D = d_a \cdot [6,007/K+ 0,64]^{1/3} \tag{2}$$

RESULTS

Figure 1, *I* shows the kinetics of the corundum formation from boehmite at 400° C in SCWF medium without additive (**Figure 1**, *I* a) and in the presence of varying amounts of M5 (**Figure 1**, *I* b, c). **Figure 1**, *II* shows linearization of kinetic curves in coordinates that
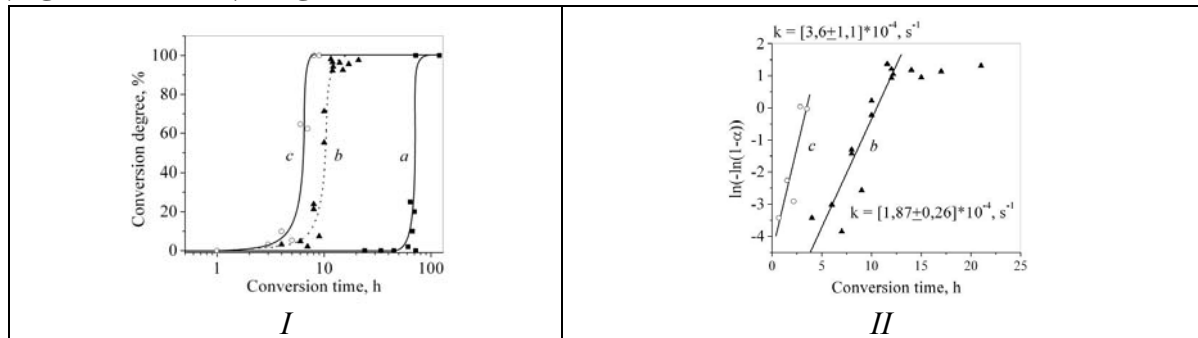
Figure 1. Kinetics of corundum formation at 400ºC and a SCWF pressure of 26.8 MPa from hydrargillite without additives (*a*) and with the addition of the M5 (*b*, *c*): *b* - K = 0.0014; *c* - K = 0.007. *I* - Kinetic curves of corundum formation. *II* - Anamorphosis of kinetic curves of corundum formation in coordinates of Equation (1).

correspond to the equation (1). The rate constant of nucleus formation can be obtained using the tilt angle of the dependence $\alpha = f(t)$ rectified in $\ln[-\ln(1-\alpha)] - t$ coordinates. It can be seen that acceleration of corundum formation occurs due to the reduction of the induction period and the increase of nucleation constant. Increasing the amount of additive to 5 times leads to rise the nucleation constant to 2 times and to reducing the time of complete conversion to 3 times. Intensification of nucleation with increasing of additive amount means that each grain of additive has inducing action.

The corundum crystals obtained in the absence of additive have isometric shape as it could be seen in SEM image (**Figure 2**, *a*). Size distribution (**Figure 2**, *a*) shows that the product consists of the three fractions. Characteristics of the resultant functions give for each faction the crystal mean size (xc_1=4.06±0.18; xc_2=18.79±0.63; xc_3=48.97±6.84 μm) and area (A1, A2, A3) under the curve, which is proportional to the number of crystals. The additive M5 has the elongated grains of irregular shape (**Figure 2**, *b*). In this case, the average size (2.82 ± 0.019 μm) was determined by analyzing the area of the particles.

| *a* | *b* | *c* | *d* |
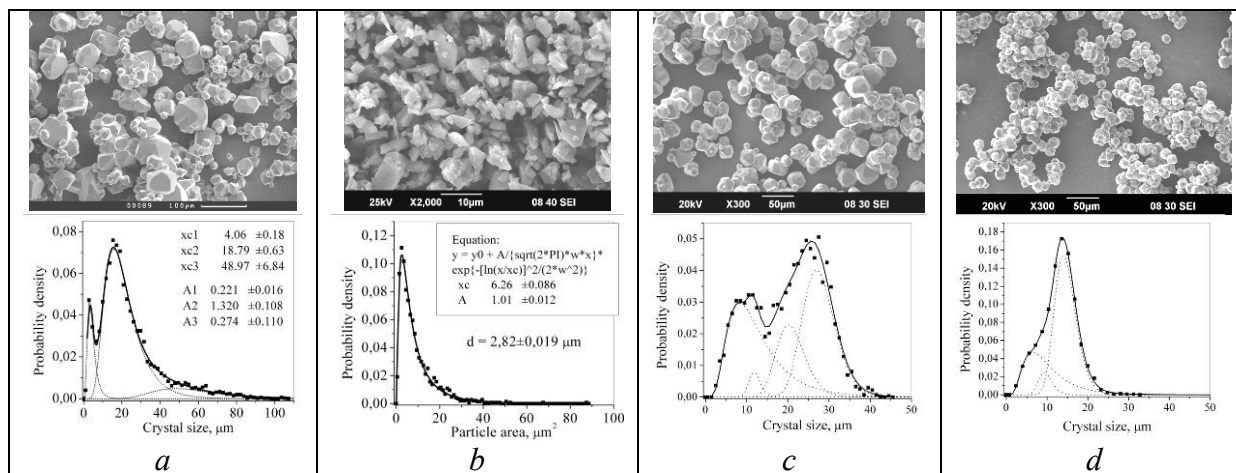
Figure 2. SEM-photo, and probability density function depending on the particle size: *a* – fine-crystalline corundum synthesized without additives, *b*- white fused alumina powder M5, *c*- corundum, formed for 21 hours at an amount of additive K = 0.0014, *d* - corundum, formed for 4 h 50 min at amount of additive K = 0.007.

The introduction of a minimum amount of additive into reaction medium leads to the appearance of the fourth fraction of larger crystals due to the grain growth of additive. Sizes and the relations of numbers of newly formed crystals of the first three fractions are changing (**Figure 2**, *c*). By increasing the amount of additive to 5 times (**Figure 2**, *d*) the distribution width and the crystal mean size of various fractions decrease. Also the number of fractions of newly formed crystals decreases from 3 to 2. The observed changes in the relative number and size of the crystals are caused by the fact that part of alumina, which is a result of dehydroxylation of boehmite, is spent on growth of grains of additive, and the residual part is spent on the nucleation and growth of new crystals: The higher the amount of additive is, the more forming alumina is spent on its grains build-up, and the remaining alumina forms less amount of new crystals, and the size of these crystals decreases. Reducing of the size of new crystals is consistent with the growth of nucleation constant. The general course of reduction of the mean size of the crystals of different fractions depending on the amount of additive is shown in **Figure 3**. Introduction of additive causes a sharp reduction in mean sizes of crystals of the three factions (**Figure 3**, *a*). With further increase of additive the crystal mean sizes decreases nonmonotonically. The values of additive amounts (0.0046 and 0.0061) marked in **Figure 3**, *a* correspond to the observed bends on curves. **Figure 3**, *b* shows the number of new crystals per a grain of additive and the ratio of number of new crystals in three fractions depending on the amount of additive. In the range of the additive amount from 0 to 0.0046 the decrease in the size of crystals is accompanied by sharp changes in the relative number of crystals of different factions. It could be seen that fraction 3 consisting of the smallest crystals at K = 0.003 disappears. The relative number of newly formed crystals of other factions passes through a maximum. Using the mass of additive and it's average grain size the dependence of the number of newly formed crystals per a grain of additive could be

recalculated into absolute number of crystals in each fraction (**Figure 3**, *c*). The number of newly formed crystals passes through maximum again in the range of additive amount from 0.0046 to 0.013, as shown in **Figure 3**, *c*. The reduction of the average crystal size in this range of amounts of additive slowed (**Figure 3**, *a*). However with the increase of additive amount the nucleation accelerated and the number of new crystals should grow. The impeding factor has spatial nature, because the increase of number grains of additive in the reaction volume leads to their nearing.
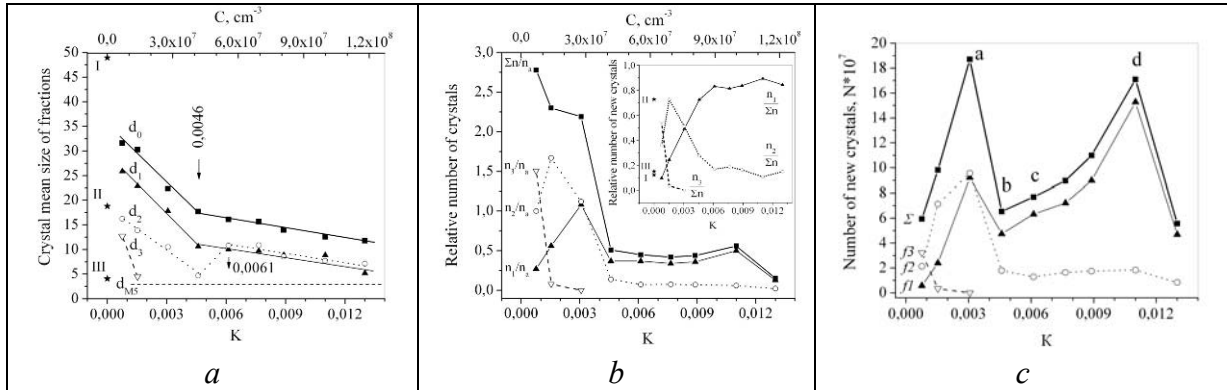
Figure 3. The dependence of the crystal mean size of different fractions (a) and the number of new crystals per grain of additive on the additive amount of M5 (b). Factions: d_0 - crystals grown from additive particles, d_1-d_3 - the newly formed crystals, dM5 − the mean size of grain of additive. Asterisks I, II and III - the crystal mean size of three fractions synthesized from hydrargillite in the absence of additive. In the inset - the proportion of new crystals of various fractions. The absolute number of new crystals as a function of the amount of grain of additive (*c*). Letters labeled amounts of additive in the reaction mixture, for which Figure 4, *II* shows the spatial situation.

One can explain the obtained results by assuming the existence of two zones of new crystals generation. In **Figure. 4. *I*** decomposition of reaction space into two zones is shown schematically. Far from the grain of additive, similarly to their absence, the nuclei are formed in the boehmite mass and new corundum crystals grow of them. This is a zone of free generation of crystals. Another zone of generation of new crystals is located around the growing crystal (d_a) in the spherical region with a diameter D_b. In this area the part of the nuclei is spent for growth of the central particle, and new crystals are formed from the remaining part. This zone can be named as sphere of buildup (SB) of the central particle. Spherical symmetry corresponds to an isometric shape of the final crystals. The final size of the forming crystals depends on the portion of boehmite per a nucleus or per each grain of additive in the surrounding space. In the sphere buildup of grain of additive some part of nuclei is spent on growth of the central particle. On the remaining nuclei the proportion of boehmite increases. As a result the size of the newly formed crystals (of fraction 1) is greater than in a remote space of free generation (of fraction 2). New crystal (of fraction 2) that appears in the space of free generation begins growing and forms the sphere buildup, absorbing some nuclei from the surrounding volume. The remaining nuclei become the source for formation of crystals of fraction 3. The space of free generation of crystals decreases with the increase of additive because the volume occupied by spheres SB increases. When the reduction of the reaction space is not compensated by an increase of nucleation rate, the number of new crystals per grain additive will begin to diminish Reducing the number of crystals of fraction 1 starts, when the spheres SB approach each other and begin to overlap

after the contact. The relative number of crystals of free generation reduced, and the proportion of crystals forming in spheres of grains buildup increases (**Figure.3**, *b* inset). Disordered packing of space by spheres SB contains interspaces of different sizes. Minimum size of interspaces at contact of spheres corresponds to tetrahedral coordination of spheres (tetrahedral interstitial site). Continuation of convergence of spheres SB leads to absorption of these interspaces.
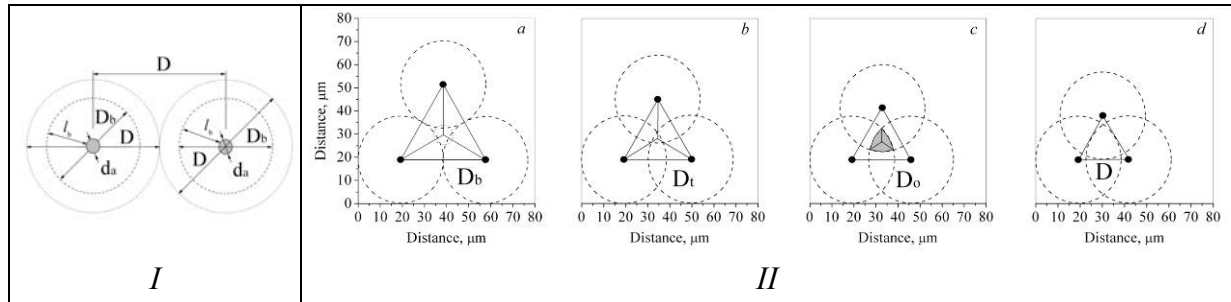
Figure 4. *I* - The scheme of distances between grains of additive in the reaction mixture :
D - the distance between the centers of grains of additive uniformly distributed in the mixture, D_b - the sphere diameter of buildup of the central particle, d_a - the grain diameter of additive, l_b - the layer thickness of buildup of the central particle.
II - The scheme of absorption of the reaction space of spheres SB with the increase of content of additive in the reaction mixture. Projections of the spheres in tetrahedral coordination on the plane of the figure are displayed. The fourth sphere, located at the apex of tetrahedron above the plane of the figure, is not shown. *a* - contact of spheres, *b* - absorption of tetrahedral interstices *c* – absorption of octahedral interstices, *d* - contact of sphere with the tetrahedron face. D_b, D_t and D_o - the distance between the grains of additive.

Figure. 4. *II* schematically shows the projection of SB spheres in tetrahedral coordination in the moment of contact, at the stages of intersection spheres and absorption of interspaces. The fourth sphere, located at the apex of tetrahedron above the plane of the figure, is not shown. Distance between grains of additive is equal to diameter D_b of spheres SB at their contact (**Figure. 4. *II***, *a*). Absorption of tetrahedral interstices finishes when the spheres SB meet in the center of tetrahedron (**Figure. 4. *II***, *b*). Using well-known representation of the close-packing of hard spheres, it is easy to show that at this point (**Figure. 4. *II***, *b*) the distance between the grains of additive $D_t = D_b/1.225$. Absorption of octahedral interstices happens when $D_o = D_b/1.414$ (**Figure. 4. *II***, *c*). After absorption of all interspaces between the spheres SB, the reaction space consists of spheres and areas intersection of spheres. The space of free generation of new crystals of fraction 2 disappears. Area of reaction space with intersection of several spheres is shown in **Figure. 4. *II***, *c* as gray figure. In the area of intersection of several spheres the density of nuclei that remain for the formation of new crystals is less than density in the nearest neighborhood. Due to this fact the crystal mean size is larger than the crystal size of fraction 1. Since the crystals of the new faction (denote 2_1) arise inside the spheres SB, the nuclei begin to be distributed between the grains of additive and crystals two fractions 1 and 2_1. Appearance of a new channel of nuclei absorption leads to a bend in dependence of the crystal mean size on the amount of additive at K = 0.0046 (**Figure. 3**, *a*). Assuming that the spheres SB meet in the center of the tetrahedron at K = 0.0046, one can accurately determine the distance D_t. According to equation 2 it is equal to 30.83 μm. The relation $D_t = D_b/1.225$ gives D_b=37.76 μm. The thickness of the layer l_b from which the grains of additive (diameter d_a = 2.82 μm, **Figure. 4.*I***) absorbs the nuclei is 17.47 microns. The distance between the centers of hard spheres in closest packing $D_o = D_b/1.414$ equals 26.7

μm. According to equation (2) this distance corresponds to the value of K = 0.0071. But, in a disordered packing of spheres the absorption of all interspaces occurs near K = 0.0061 and a greater distance between the grains additive D ≥ 28.06 μm. This result is obvious and corresponds to the fact that the size of interspace of disordered packing of spheres is larger than the size of octahedral holes in the closest packing of hard spheres. Using the proposed interpretation of the results, one can determine the spatial situation in point of the second maximum at K = 0.011 in **Figure 3**, *c* and K = 0.013 at the sharp decline in the number of new crystals. The distance between the grains of additive at K = 0.011 is 23.06 μm. It is practically equal to the distance between the spheres of SB at contact of sphere with face of the tetrahedron (D = 23.12 μm, **Figure 4**, d). Continuation of convergence of spheres SB leads to overlap of the areas of spheres intersection, and all the reaction space absorbs the area where generation of crystals of fraction 2_1 occurs. Continuation of convergence of spheres SB leads to overlapping of the intersection areas, and the area of generation crystals of fraction 2_1 absorbs the all reaction space. Under these conditions, the space of generation of new crystals fraction 1 disappears.

CONCLUSION

The introduction of crystalline particles into the reaction medium leads to the increase in nucleation rate in the whole reaction space and accelerates transformation hydrargillite-boehmite-corundum in water fluid of low density. Alumina, which appears as a result of dehydroxylation of boehmite, grows on grains of additive and is formed as the new crystals. The distance between the grains of additive affects the formation of new crystals. With the increase of additive in the investigated range the proportion of alumina that was buildup on the grains of additive increases from about 0.5 to 0.98. The mean crystal size of fractions and the number of new corundum crystals per grain of additive nonmonotonically decrease. To explain the results a model for the generation and growth of corundum crystals has been developed. According to this model the buildup of introduced corundum particles occurs through the absorption of the part of nuclei produced in the surrounding layer of boehmite. It is established for the grain of additive with an average size of 2.82 μm that the diameter of the sphere of nuclei collecting and the distance from the grain to boundary of sphere are 37.76 μm and 17.47 μm, respectively. New corundum crystals are formed from the remaining part of the nuclei inside the sphere and of all the nuclei beyond. With the increase of the additive amount the spheres of grain growth occupy whole reaction space and begin overlapping. Completion of the various stages of the space filling causes the appearance of singular points on the dependences of sizes and numbers of crystals on the amount of additive.

REFERENCES

[1] LASAREV, V.B., PANASYUK, G.P., DANCHEVSKAYA, M.N., Zh. VKhO im. D.I. Mendeleeva, Vol. 36, **1991**, p. 706
[2] IVAKIN, Yu.D., DANCHEVSKAYA, M.N., OVCHINNIKOVA, O.G., MURAV'EVA, G.P., KREISBERG, V.A. Russian Journal of Physical Chemistry B, Vol. 3, **2009**, No. 7, p. 1019
[3] G., YAMAGUCHI, H., YANAGIDA, Factors Determining the Grain Size of Corundum, Vol. 36(9), **1963**, p. 1155
[4] SUCHANEK W.L., J. Amer. Ceram.Soc., Vol. 93(2), **2010**, p. 399
[5] N.S., BELL, S-B., CHO, J.H. ADAIR, J. Amer. Ceram.Soc., Vol. 81(6), **1998**, p. 1411
[6] J.L., MCARDLE, G.L., MESSING, L., TIETZ, C.B., CARTER, J. Am. Ceram. Soc., Vol. 72, **1989**, p. 864
[7] P., TROPPER, C.E., MANNING, Chemical Geology, Vol. 240, **2007**, p. 54
[8] J.D., BERNAL, J., MASON, Nature Vol. 188, **1960**, p. 910